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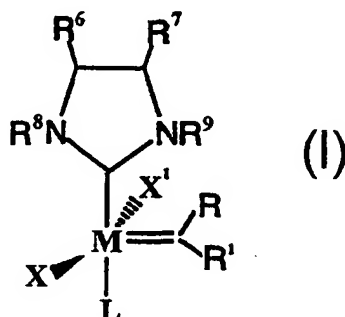
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(54) Title: IMIDAZOLIDINE-BASED METAL CARBENE METATHESIS CATALYSTS



WO 00/71554 A2

(57) Abstract: The present invention relates to novel metathesis catalysts with an imidazolidine-based ligand and to methods for making and using the same. The inventive catalysts are of formula (I) wherein: M is ruthenium or osmium; X and X¹ are each independently an anionic ligand; L is a neutral electron donor ligand; and, R, R¹, R⁶, R⁷, R⁸ and R⁹ are each independently hydrogen or a substituent selected from the group consisting of C₁-C₂₀ alkyl, C₂-C₂₀ alkenyl, C₂-C₂₀ alkynyl, aryl, C₁-C₂₀ carboxylate, C₁-C₂₀ alkoxy, C₂-C₂₀ alkenyloxy, C₂-C₂₀ alkynyloxy, aryloxy, C₂-C₂₀ alkoxycarbonyl, C₁-C₂₀ alkylthiol, aryl thiol, C₁-C₂₀ alkylsulfonyl and C₁-C₂₀ alkylsulfinyl, the substituent optionally substituted with one or more moieties selected from the group consisting of C₁-C₁₀ alkyl, C₁-C₁₀ alkoxy, aryl, and a functional group selected from the group consisting of hydroxyl, thiol thioether, ketone, aldehyde, ester, ether, amine, imine, amide, nitro, carboxylic acid, disulfide, carbonate, isocyanate, carbodiimide, carboalkoxy, carbamate, and halogen. The inclusion of an imidazolidine ligand to the previously described ruthenium or osmium catalysts has been found to dramatically improve the properties of these complexes. The inventive catalysts maintain the functional group tolerance of previously described ruthenium complexes while having enhanced metathesis activity that compares favorably to prior art tungsten and molybdenum systems.

IMIDAZOLIDINE-BASED METAL CARBENE METATHESIS CATALYSTS

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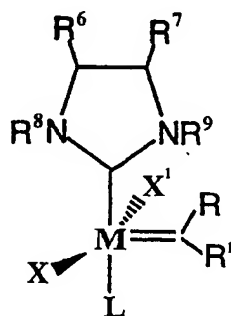
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BACKGROUND

Metathesis catalysts have been previously described by for example, United States
Patents Nos. 5,312,940, 5,342,909, 5,728,917, 5,750,815, 5,710,298, and 5,831,108 and
15 PCT Publications WO 97/20865 and WO 97/29135 which are all incorporated herein by
reference. These publications describe well-defined single component ruthenium or
osmium catalysts that possess several advantageous properties. For example, these
catalysts are tolerant to a variety of functional groups and generally are more active than
previously known metathesis catalysts. In an unexpected and surprising result, the
20 inclusion of an imidazolidine ligand in these metal-carbene complexes has been found to
dramatically improve the already advantageous properties of these catalysts. For
example, the imidazolidine-based catalysts of the present invention exhibit increased
activity and selectivity not only in ring closing metathesis ("RCM") reactions, but also in
other metathesis reactions including cross metathesis ("CM") reactions, reactions of
25 acyclic olefins, and ring opening metathesis polymerization ("ROMP") reactions.

SUMMARY

The present invention relates to novel metathesis catalysts with an imidazolidine-based ligand and to methods for making and using the same. The inventive catalysts are of the formula



wherein:

M is ruthenium or osmium;

X and X¹ are each independently an anionic ligand;

10 L is a neutral electron donor ligand; and,

R, R¹, R⁶, R⁷, R⁸, and R⁹ are each independently hydrogen or a substituent selected from the group consisting of C₁-C₂₀ alkyl, C₂-C₂₀ alkenyl, C₂-C₂₀ alkynyl, aryl, C₁-C₂₀ carboxylate, C₁-C₂₀ alkoxy, C₂-C₂₀ alkenyloxy, C₂-C₂₀ alkynyloxy, aryloxy, C₂-C₂₀ alkoxycarbonyl, C₁-C₂₀ alkylthiol, aryl thiol, C₁-C₂₀ alkylsulfonyl and C₁-C₂₀ alkylsulfinyl. Optionally, each of the R, R¹, R⁶, R⁷, R⁸, and R⁹ substituent group may be substituted with one or more moieties selected from the group consisting of C₁-C₁₀ alkyl, C₁-C₁₀ alkoxy, and aryl which in turn may each be further substituted with one or more groups selected from a halogen, a C₁-C₅ alkyl, C₁-C₅ alkoxy, and phenyl. Moreover, any of the catalyst ligands may further include one or more functional groups. Examples of suitable functional groups include but are not limited to: hydroxyl, thiol, thioether, ketone, aldehyde, ester, ether, amine, imine, amide, nitro, carboxylic acid, disulfide, carbonate, isocyanate, carbodiimide, carboalkoxy, carbamate, and halogen. The inclusion of an imidazolidine ligand to the previously described ruthenium or osmium catalysts has been found to dramatically improve the properties of these complexes. Imidazolidine ligands are also referred to as 4,5-dihydro-imidazole-2-ylidene ligands. Because the imidazolidine-based complexes are extremely active, the amount of catalysts that is required is significantly reduced.

BRIEF DESCRIPTION OF THE DRAWINGS

Figure 1 compares the ROMP activity of COD of representative catalysts of the present invention with previously described metathesis catalysts as determined by ^1H NMR spectroscopy. The reactions were performed at 20°C with CD_2Cl_2 as solvent, a monomer/catalyst ratio of 300, and a catalyst concentration of 0.5 mM.

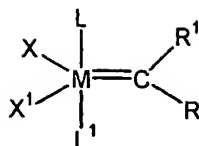
Figure 2 compares the ROMP activity of COE of representative catalysts of the present invention with previously described metathesis catalysts as determined by ^1H NMR spectroscopy. The reactions were performed at 20°C with CD_2Cl_2 as solvent, a monomer/catalyst ratio of 300, and a catalyst concentration of 0.5 mM.

Figure 3 compares the ROMP activity of COD at an elevated temperature of representative catalysts of the present invention with previously described metathesis catalysts as determined by ^1H NMR spectroscopy. The reactions were performed at 55°C with CD_2Cl_2 as solvent, a monomer/catalyst ratio of 300, and a catalyst concentration of 0.5 mM.

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

The present invention generally relates to ruthenium and osmium carbene catalysts for use in olefin metathesis reactions. More particularly, the present invention relates to imidazolidine-based ruthenium and osmium carbene catalysts and to methods for making and using the same. The terms "catalyst" and "complex" herein are used interchangeably.

Unmodified ruthenium and osmium carbene complexes have been described in United States Patents Nos. 5,312,940, 5,342,909, 5,728,917, 5,750,815, and 5,710,298, all of which are incorporated herein by reference. The ruthenium and osmium carbene complexes disclosed in these patents all possess metal centers that are formally in the +2 oxidation state, have an electron count of 16, and are penta-coordinated. These catalysts are of the general formula



wherein:

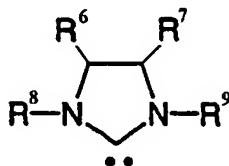
M is ruthenium or osmium;

X and X¹ are each independently any anionic ligand;

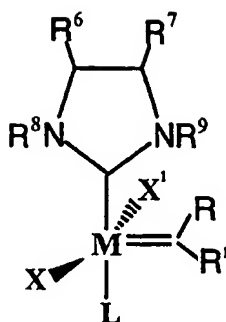
5 L and L¹ are each independently any neutral electron donor ligand;

R and R¹ are each independently hydrogen or a substituent selected from the group consisting of C₁-C₂₀ alkyl, C₂-C₂₀ alkenyl, C₂-C₂₀ alkynyl, aryl, C₁-C₂₀ carboxylate, C₁-C₂₀ alkoxy, C₂-C₂₀ alkenyloxy, C₂-C₂₀ alkynyloxy, aryloxy, C₂-C₂₀ alkoxycarbonyl, C₁-C₂₀ alkylthiol, aryl thiol, C₁-C₂₀ alkylsulfonyl and C₁-C₂₀ alkylsulfinyl. Optionally,
 10 each of the R or R¹ substituent group may be substituted with one or more moieties selected from the group consisting of C₁-C₁₀ alkyl, C₁-C₁₀ alkoxy, and aryl which in turn may each be further substituted with one or more groups selected from a halogen, a C₁-C₅ alkyl, C₁-C₅ alkoxy, and phenyl. Moreover, any of the catalyst ligands may further include one or more functional groups. Examples of suitable functional groups include
 15 but are not limited to: hydroxyl, thiol, thioether, ketone, aldehyde, ester, ether, amine, imine, amide, nitro, carboxylic acid, disulfide, carbonate, isocyanate, carbodiimide, carboalkoxy, carbamate, and halogen.

The catalysts of the present invention are as described above except that L¹ is an
 20 unsubstituted or substituted imidazolidine,



resulting in a complex of the general formula



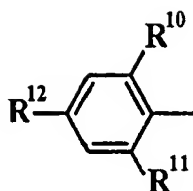
wherein:

- R^6 , R^7 , R^8 , and R^9 are each independently hydrogen or a substituent selected from the group consisting of C₁-C₂₀ alkyl, C₂-C₂₀ alkenyl, C₂-C₂₀ alkynyl, aryl, C₁-C₂₀ carboxylate, C₁-C₂₀ alkoxy, C₂-C₂₀ alkenyloxy, C₂-C₂₀ alkynyloxy, aryloxy, C₂-C₂₀ alkoxy carbonyl, C₁-C₂₀ alkylthiol, aryl thiol, C₁-C₂₀ alkylsulfonyl and C₁-C₂₀ alkylsulfinyl. Imidazolidine ligands are also referred to as 4,5-dihydro-imidazole-2-ylidene ligands.
- 10 In preferred embodiments of the inventive catalysts, the R substituent is hydrogen and the R¹ substituent is selected from the group consisting of C₁-C₂₀ alkyl, C₂-C₂₀ alkenyl, and aryl. In even more preferred embodiments, the R¹ substituent is phenyl or vinyl, optionally substituted with one or more moieties selected from the group consisting of C₁-C₅ alkyl, C₁-C₅ alkoxy, phenyl, and a functional group. In especially preferred
- 15 embodiments, R¹ is phenyl or vinyl substituted with one or more moieties selected from the group consisting of chloride, bromide, iodide, fluoride, -NO₂, -NMe₂, methyl, methoxy and phenyl. In the most preferred embodiments, the R¹ substituent is phenyl or -C=C(CH₃)₂.
- 20 In preferred embodiments of the inventive catalysts, L is selected from the group consisting of phosphine, sulfonated phosphine, phosphite, phosphinite, phosphonite, arsine, stibine, ether, amine, amide, imine, sulfoxide, carboxyl, nitrosyl, pyridine, and thioether. In more preferred embodiments, L is a phosphine of the formula PR³R⁴R⁵, where R³, R⁴, and R⁵ are each independently aryl or C₁-C₁₀ alkyl, particularly primary
- 25 alkyl, secondary alkyl or cycloalkyl. In the most preferred embodiments, L is each selected from the group consisting of -P(cyclohexyl)₃, -P(cyclopentyl)₃, -P(isopropyl)₃, and -P(phenyl)₃.

In preferred embodiments of the inventive catalysts, X and X¹ are each independently hydrogen, halide, or one of the following groups: C₁-C₂₀ alkyl, aryl, C₁-C₂₀ alkoxide, aryloxide, C₃-C₂₀ alkylidicketonate, arylidicketonate, C₁-C₂₀ carboxylate, arylsulfonate, C₁-C₂₀ alkylsulfonate, C₁-C₂₀ alkylthiol, aryl thiol, C₁-C₂₀ alkylsulfonyl, or C₁-C₂₀ alkylsulfinyl. Optionally, X and X¹ may be substituted with one or more moieties selected from the group consisting of C₁-C₁₀ alkyl, C₁-C₁₀ alkoxy, and aryl which in turn may each be further substituted with one or more groups selected from halogen, C₁-C₅ alkyl, C₁-C₅ alkoxy, and phenyl. In more preferred embodiments, X and X¹ are halide, benzoate, C₁-C₅ carboxylate, C₁-C₅ alkyl, phenoxy, C₁-C₅ alkoxy, C₁-C₅ alkylthiol, aryl thiol, aryl, and C₁-C₅ alkyl sulfonate. In even more preferred embodiments, X and X¹ are each halide, CF₃CO₂, CH₃CO₂, CFH₂CO₂, (CH₃)₃CO, (CF₃)₂(CH₃)CO, (CF₃)(CH₃)₂CO, PhO, MeO, EtO, tosylate, mesylate, or trifluoromethanesulfonate. In the most preferred embodiments, X and X¹ are each chloride.

In preferred embodiments of the inventive catalysts, R⁶ and R⁷ are each independently hydrogen, phenyl, or together form a cycloalkyl or an aryl optionally substituted with one or more moieties selected from the group consisting of C₁-C₁₀ alkyl, C₁-C₁₀ alkoxy, aryl, and a functional group selected from the group consisting of hydroxyl, thiol, thioether, ketone, aldehyde, ester, ether, amine, imine, amide, nitro, carboxylic acid, disulfide, carbonate, isocyanate, carbodiimide, carboalkoxy, carbamate, and halogen; and R⁸ and R⁹ are each is independently C₁-C₁₀ alkyl or aryl optionally substituted with C₁-C₅ alkyl, C₁-C₅ alkoxy, aryl, and a functional group selected from the group consisting of hydroxyl, thiol, thioether, ketone, aldehyde, ester, ether, amine, imine, amide, nitro, carboxylic acid, disulfide, carbonate, isocyanate, carbodiimide, carboalkoxy, carbamate, and halogen.

In more preferred embodiments, R⁶ and R⁷ are both hydrogen or phenyl, or R⁶ and R⁷ together form a cycloalkyl group; and R⁸ and R⁹ are each either substituted or unsubstituted aryl. Without being bound by theory, it is believed that bulkier R⁸ and R⁹ groups result in catalysts with improved characteristics such as thermal stability. In especially preferred embodiments, R⁸ and R⁹ are the same and each is independently of the formula

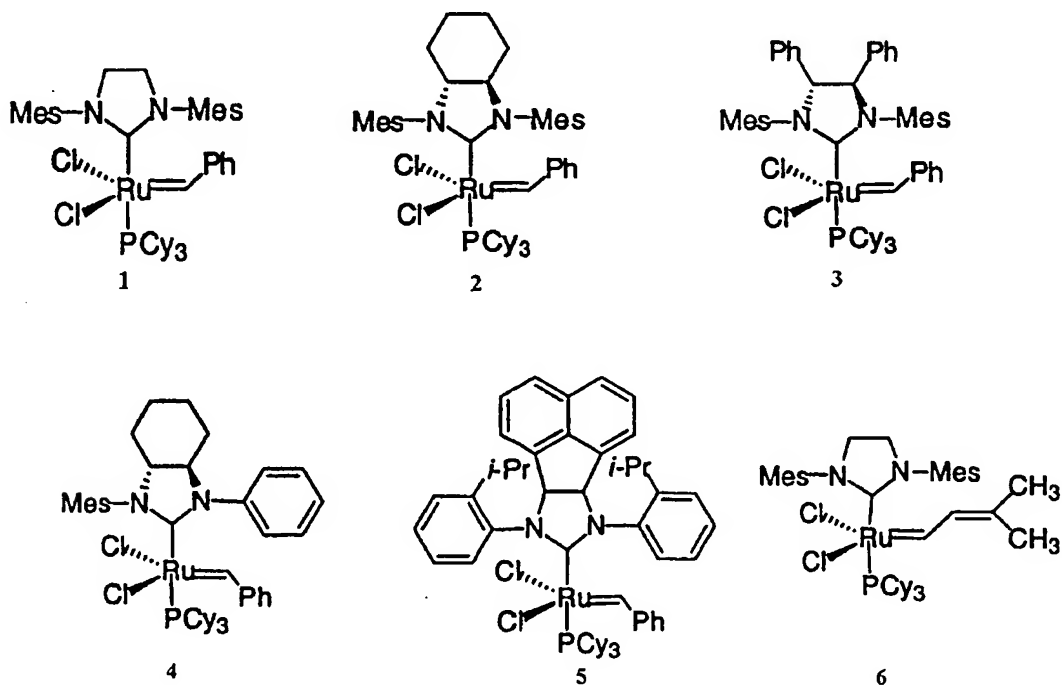


wherein:

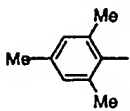
- R^{10} , R^{11} , and R^{12} are each independently hydrogen, C_1 - C_{10} alkyl, C_1 - C_{10} alkoxy, aryl, or a functional group selected from hydroxyl, thiol, thioether, ketone, aldehyde, ester, ether, amine, imine, amide, nitro, carboxylic acid, disulfide, carbonate, isocyanate, carbodiimide, carboalkoxy, carbamate, and halogen. In especially preferred embodiments, R^{10} , R^{11} , and R^{12} are each independently selected from the group consisting of hydrogen, methyl, ethyl, propyl, isopropyl, hydroxyl, and halogen. In the most preferred embodiments, R^{10} , R^{11} , and R^{12} are the same and are each methyl.

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Examples of the most preferred embodiments of the present invention include:



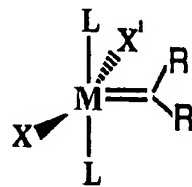
15



wherein Mes is (also known as "mesityl"); *i*-Pr is isopropyl; and PCy_3 is -P(cyclohexyl)₃.

Synthesis

In general, the catalysts of the present invention are made by contacting an imidazolidine

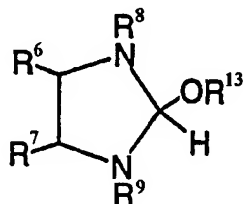


with a previously described ruthenium/osmium catalyst

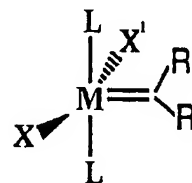
whereby the

- 5 imidazolidine replaces one of the L ligands. The imidazolidine may be made using any suitable method.

In preferred embodiments, the method for making the inventive catalysts comprises contacting an imidazolidine of the general formula



with



wherein:

M is ruthenium or osmium;

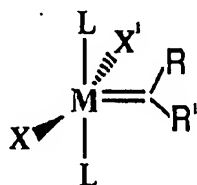
X and X' are each independently an anionic ligand;

L is a neutral electron donor ligand;

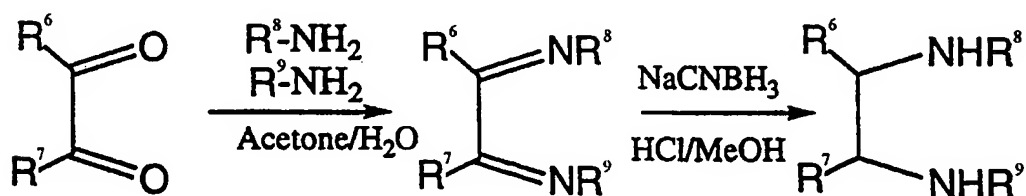
- 15 R, R¹, R⁶, R⁷, R⁸, and R⁹ are each independently hydrogen or a substituent selected from the group consisting of C₁-C₂₀ alkyl, C₂-C₂₀ alkenyl, C₂-C₂₀ alkynyl, aryl, C₁-C₂₀ carboxylate, C₁-C₂₀ alkoxy, C₂-C₂₀ alkenyloxy, C₂-C₂₀ alkynyloxy, aryloxy, C₂-C₂₀ alkoxycarbonyl, C₁-C₂₀ alkylthiol, aryl thiol, C₁-C₂₀ alkylsulfonyl and C₁-C₂₀ alkylsulfinyl, the substituent optionally substituted with one or more moieties selected
- 20 from the group consisting of C₁-C₁₀ alkyl, C₁-C₁₀ alkoxy, aryl, and a functional group selected from the group consisting of hydroxyl, thiol, thioether, ketone, aldehyde, ester, ether, amine, imine, amide, nitro, carboxylic acid, disulfide, carbonate, isocyanate, carbodiimide, carboalkoxy, carbamate, and halogen; and,
- R¹³ is C₁-C₂₀ alkyl or aryl.

If desired, the contacting step may be performed in the presence of heat. Typically, the replacement reaction whereby the imidazolidine displaces one of the L ligands occurs in about 10 minutes in the presence of heat.

- 5 The imidazolidine may be synthesized by contacting a diamine with a salt to form an imidazolium salt; and then contacting the imidazolium salt with a base (preferably an alkoxide) to make the imidazolidine in a form suitable for reacting with

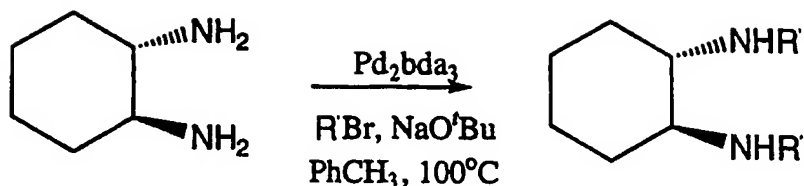


- 10 One embodiment for the synthetic method is as follows. First, a diketone is contacted with a primary amine ($R-NH_2$ wherein $R^8 = R^9$) or amines (R^8-NH_2 and R^9-NH_2) to form a diimine which is then reduced to form a diamine.



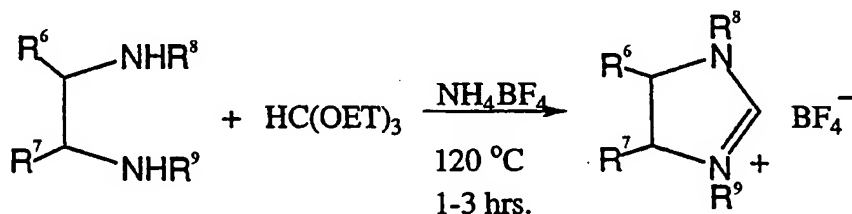
In preferred embodiments, R^8 and R^9 are the same and are each independently C_1 - C_{10}

- 15 alkyl or aryl optionally substituted with C_1 - C_5 alkyl, C_1 - C_5 alkoxy, aryl, and a functional group selected from the group consisting of hydroxyl, thiol, thioether, ketone, aldehyde, ester, ether, amine, imine, amide, nitro, carboxylic acid, disulfide, carbonate, isocyanate, carbodiimide, carboalkoxy, carbamate, and halogen.
- 20 When R^6 and R^7 together form a cycloalkyl and R^8 and R^9 are the same, the following alternate protocol may be used to make the diamine intermediate of the present invention:



- wherein R' represents both R⁸ and R⁹ since R⁸ = R⁹. Because a number of optically active primary cycloalkyldiamines are commercially available, this protocol may be used to synthesize optically active imidazolidine ligands. In addition, chiral metathesis
- 5 complexes are also possible.

The diamine intermediate is used to prepare an imidazolium salt. In one embodiment, ammonium tetrafluoroborate may be used.



- 10 The resulting imidazolium salt is then reacted with a base to make the imidazolidine.



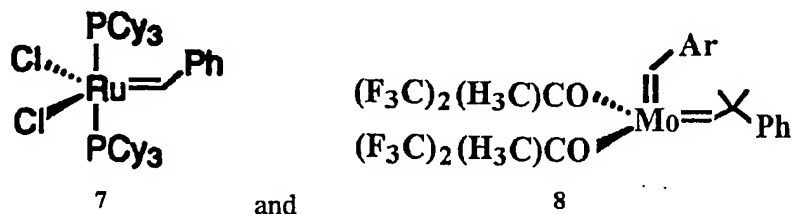
Representative examples of suitable bases include the *t*-BuOK/THF and MeONa/MeOH.

15 Metathesis Reactions

- The catalysts of the present invention may be used for any metathesis reaction (*i.e.* ring opening metathesis polymerization, ring closing metathesis, cross metathesis, etc.) by contacting the inventive catalysts with an appropriate olefin. Any olefin may be used and as used herein an olefin is a substituted or unsubstituted alkene and is any compound
- 20 including cyclic compounds that possess a carbon-carbon double bond. Unlike previously described metathesis catalysts, the inventive complexes can initiate reactions involving even highly substituted olefins such as tri and tetra substituted olefins (*e.g.*,

$R^1R^2C=CR^3R^4$ wherein R^1 , R^2 , R^3 , and R^4 are independently each a hydrogen or a non-hydrogen moiety) and olefins bearing electron withdrawing groups.

In general, the method for performing a metathesis reaction comprises contacting a
5 suitable olefin with a catalyst of the present invention. To date, the most widely used
catalysts for ROMP and other metathesis reactions are



wherein PCy₃ is -P(cyclohexyl)₃ and Ar is C₆H₃-2,6-(ⁱPR). The molybdenum catalyst 8 displays much higher activity than the ruthenium catalyst 7, thus permitting polymerization of many sterically hindered or electronically deactivated cyclic olefins. However, the ruthenium catalyst 7 is stable under ambient conditions and tolerates a much larger range of protic and polar functional groups such as alcohols, acids and aldehydes. The catalysts of the present invention combine the best features of both complexes 7 and 8. In particular, the inventive imidazolidine catalysts rival and often exceed the activity of molybdenum complex 8 while maintaining the stability and functional group compatibility of ruthenium complex 7.

The enhanced properties of the inventive catalysts are illustrated by a series of experiments. For example, Table 1 contains representative results comparing the activities of two representative catalysts (1 and 2) of the present invention with complex 7 in several ring closing metathesis reactions with an acyclic olefin.

Table 1: Results of the RCM with 5 mol% cat. in 0.05M CH₂Cl₂ at reflux

Entry	Substrate	Product	% Yield (Time, min) with catalyst 7	% Yield (Time, min) with catalyst 1	% Yield (Time, min) with catalyst 2 ^a
1			100 (<30)	100 (5)	100 (8)
2			25 (12) 82 (30)	100 (8)	100 (12)
3			N.R. (60)	100 (60)	65 (20) 92 (12hrs)
4			N.R. (90)	N.R.	14 (100) 47 (36 hrs)
5			N.R. (90)	90 (90)	80 (60) 92 (12 hrs)
6			39 ^b (60)	35 ^c (60)	55 ^c (60)

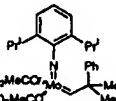

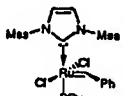
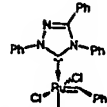






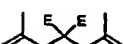





E = CO₂Et; ^a in CD₂Cl₂, conversion determined by ¹H NMR, ^b E:Z = 1.6:1, ^c E:Z = 2.0:1

As it can be seen, the ring closure of diethyl diallylmalonate ester (entry 1) is completed in less than 10 minutes at 40 °C with both complexes 1 and 2 while complex 7 requires about 30 minutes. The increased activity of complexes 1 and 2 is most apparent in RCM reactions with more sterically demanding olefins. For example, 2-*tert*-butyl-diethyl diallyl malonate ester (entry 3) can be cyclized with 5 mol% of catalyst 1 in one hour, with 5 mol% of catalyst 2 in twelve hours, while the corresponding reaction with 5 mol% of catalyst 7 does not yield any significant amount of cyclized product. Similarly,

tetrasubstituted olefins (entries 4 and 5) can be prepared in moderate to excellent yields using complexes 1 and 2.

Table 2 shows the results of the same RCM experiments for previously described
5 metathesis catalysts including complexes 7 and 8.

TABLE 2: RCM ACTIVITY COMPARISONS

Substrate E = CO ₂ Et	Product	 (F ₃ C) ₂ MeCO ₂ N(Me)C(Ph) ₂ 5 mol%, 0.10M C ₆ D ₆ , 85°C	 5 mol%, 0.05M CD ₃ Cl ₂ , 40°C	 5 mol%, 0.05M CD ₃ Cl ₂ , 40°C	 5 mol%, 0.05M CD ₃ Cl ₂ , 40°C
		---	30 min 100%	30 min 100%	30 min 100%
		24 hrs 100%	30 min 82%	30 min 100%	---
		24 hrs 96%	no reaction	60 min 100%	30 min 85%
		24 hrs 96%	no reaction	90 min 40%	30 min 53%
		24 hrs 61%	no reaction	90 min 85%	30 min 82%
		---	60 min 39% E:Z=1.6:1	60 min 55% E:Z=2.0:1	30 min 73% E:Z=2.3:1

10 Since complexes 1 and 2 are much more reactive than complex 7, the use of lower catalysts loading for RCM reactions was investigated. The ring closure of diethyl diallylmalonate under the reaction conditions listed in Table 1 was conducted using 0.1, 0.05, and 0.01 mol% of catalysts (1 or 2) with respect to the substrate. In the first case, quantitative conversions within one hour were observed with both catalysts; in the second
15 case, the conversion were quantitative with 1 (one hour) and 94% with 2 (three hours). In the third case, the conversions were nearly zero, which indicates that 0.01 mol% is at the lower limit of the catalyst loading for this type of RCM reactions.

- The catalysts of the present invention are also useful for ROMP reactions. In general, the method involves contacting the catalyst with a cyclic olefin. The cyclic olefin substrate may be a single cyclic olefin or a combination of cyclic olefins (*i.e.* a mixture of two or more different cyclic olefins). The cyclic olefins may be strained or unstrained,
- 5 monocyclic or polycyclic, and may optionally include hetero atoms and/or one or more functional groups. Suitable cyclic olefins include but are not limited to norbornene, norbornadiene, dicyclopentadiene, cyclopentene, cycloheptene, cyclooctene, cyclooctadiene, cyclododecene, 7-oxanorbornene, 7-oxanorbornadiene, and derivatives therefrom. Illustrative examples of suitable functional groups include but are not limited
- 10 to hydroxyl, thiol, ketone, aldehyde, ester, ether, amine, imine, amide, nitro, carboxylic acid, disulfide, carbonate, isocyanate, carbodiimide, carboalkoxy, and halogen. Preferred cyclic olefins include norbornene and dicyclopentadiene and their respective homologs and derivatives. The most preferred cyclic olefin is dicyclopentadiene ("DCPD").
- 15 The ROMP reaction may occur either in the presence or absence of solvent and may optionally include formulation auxiliaries. Known auxiliaries include antistatics, antioxidants, light stabilizers, plasticizers, dyes, pigments, fillers, reinforcing fibers, lubricants, adhesion promoters, viscosity-increasing agents and demolding enhancers. Illustrative examples of fillers for improving the optical physical, mechanical and
- 20 electrical properties include glass and quartz in the form of powders, beads and fibers, metal and semi-metal oxides, carbonates (*i.e.* MgCO_3 , CaCO_3), dolomite, metal sulfates (such as gypsum and barite), natural and synthetic silicates (*i.e.* zeolites, wollastonite, feldspars), carbon fibers, and plastics fibers or powders.
- 25 The inventive catalysts' utility in ROMP reactions was demonstrated with polymerizations both *endo*- and *exo*-DCPD. Exposure of neat DCPD to catalyst 1 (10,000:1) yielded within seconds a hard, highly-crosslinked material. In fact, catalyst loadings as low as 130,000:1 have been used to make high-quality poly-DCPD product. In contrast, previously described ruthenium and osmium catalysts such as 7, required
- 30 loadings of 7,000:1 to obtain similar poly-DCPD product.

As demonstrated by the synthesis of telechelic polybutadiene by chain transfer ROMP, the inventive catalysts are also extremely active in the polymerization of unstrained cyclic

olefins. For example, with a catalyst loading of about 12,000:1 (monomer to catalyst 1), the yield of telechelic polymers is higher (65%) than that using the bis-phosphine complex 7 at much lower monomer to catalyst ratio of 2,000:1 (50%).

- 5 High activities were also observed in the crossmetathesis of acyclic olefins. As an example, the cross metathesis of 9-decen-1-yl benzoate with *cis*-2-buten-1,4-diol diacetate catalyzed by 2 gave a high yield (80%) and a higher amount of the *trans* isomer (E:Z = 9:1) compared to that when the corresponding bis-phosphine complex 7 was used (E:Z = 4.7:1).

10

EXAMPLE 1

A synthetic protocol for a representative example of an imidazolidine ligand is as follows. Other imidazolidine ligands are made analogously.

15 Preparation of 1,2-dimesityl ethylene diimine:

A 300 mL round bottom flask was charged with acetone (50 mL), water (100 mL) and mesityl amine (10.0 g, 74 mmol). The solution was cooled to 0°C and a solution of 40% glyoxal in water (5.38 g, 37 mmol) was added slowly. The reaction mixture was allowed to warm up to room temperature slowly and was stirred for additional 8 hours. The
20 yellow precipitate formed was filtered off, briefly washed with cold acetone and air-dried to yield 1,2-dimesityl ethylene diimine.

Preparation of 1,2-dimesityl ethylene diamine:

(a) with H₂, Pd/C: A 50 mL round bottom flask was charged with 1,2-dimesityl
25 ethylene diimine (300 mg, 1.01 mmol) and ethanol (20 mL). 10% Pd/C (30 mg) was added and a hydrogen balloon was attached via a needle. TLC indicated complete spot-to-spot conversion within 4 hours. The Pd catalyst was filtered off and the volatiles were pumped off in vacuo to yield 1,2-dimesityl ethylene diamine.

(b) with NaCNBH₃: A 300 mL round bottom flask was charged with 1,2-dimesityl
30 ethylene diimine (3.8 g, 13 mmol), methanol (100 mL) and NaCNBH₃ (4.92 g, 78 mmol). Concentrated HCl was added dropwise to maintain the pH below 4, and the reaction was stirred at room temperature for 20 hours (overnight). The solution was then diluted with 50 mL water, made basic with NaOH, and extracted thoroughly with CH₂Cl₂. The

organic layer was dried over MgSO_4 , filtered and the solvent was removed in vacuo to yield 1,2-dimesityl ethylene diamine (95% yield).

Preparation of 1,3-dimesityl-4,5-dihydro-imidazolium tetrafluoroborate:

- 5 A round bottom flask was charged with 1,2-dimesityl ethylene diamine (3.8 g, 12.8 mmol), triethyl orthoformate (15 mL) and ammonium tetrafluoroborate (1.35 g, 12.8 mmol). The reaction mixture was stirred at 120°C for 4 hours at which time TLC indicated complete conversion. Volatiles were removed in vacuo and the product was used as prepared or it could be purified further by recrystallization from ethanol/hexanes.
- 10

EXAMPLE 2

Synthesis of $\text{Cl}_2\text{Ru}(=\text{CHPh})(\text{PCy}_3)(1,3\text{-dimesityl-4,5-dihydro-2-imidazole})$:

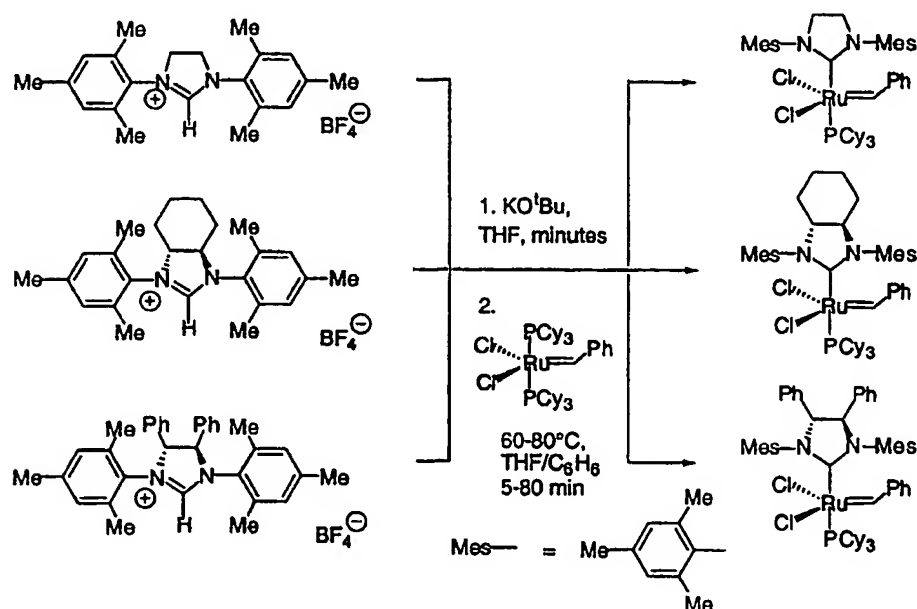
- The imidazolidine ligand synthesized as detailed in Example 1 is used to prepare the
- 15 corresponding imidazolidine catalyst ("complex 1") of the present invention. A 100-mL flame dried Schlenk flask equipped with a magnetic stir bar was charged with 1,3-dimesityl-4,5-dihydro-imidazolium tetrafluoroborate (394 mg, 1.0 mmol, 1 equiv.) and dry THF (20 mL) under nitrogen atmosphere. To this suspension, potassium *tert*-butoxide (122 mg, 1.0 mmol, 1 equiv.) was slowly added at room temperature. The
- 20 tetrafluoroborate salt was dissolved immediately to give a yellow solution. The reaction mixture was allowed to stir at room temperature for one hour, followed by cannula transferring the reaction solution into another 100-mL dry Schlenk flask under Argon. The solvent was evaporated under high vacuum, followed by adding dry benzene (25 mL) and $\text{RuCl}_2(=\text{CHPh})(\text{PCy}_3)_2$ (700 mg, 0.85 mmol, 0.85 equiv.). The reaction mixture was
- 25 heated at 80 °C for 90 minutes. When the reaction was complete indicated by NMR, the volatiles were removed under high vacuum and the residue was washed by dry methanol (20 ml x 4) to give pinkish brown microcrystalline solid (404 mg) in 56% yield. : ^1H NMR (CD_2Cl_2 , 400 MHz) δ 19.16 (s, 1H), 7.37-7.05 (m, 9H), 3.88 (s, 4H), 2.56-0.15 (m, 51H); ^{31}P NMR (CD_2Cl_2 , 161.9 MHz) δ 31.41; HRMS (FAB) $\text{C}_{45}\text{H}_{65}\text{Cl}_2\text{N}_2\text{PRu} [\text{M}^+]$
- 30 848.3306, found 848.3286.

EXAMPLE 3

Synthesis of complex 2

A second example of synthetic protocol for making the inventive catalysts (complex 2) follows. 1,3-dimesityl-trans-hexahydrobenzoimidazolium tetrafluoroborate (272 mg, 0.61 mmol, 1.0 equiv.) was suspended in anhydrous tetrahydrofuran ("THF"; 5 mL) under inert atmosphere. To this suspension, potassium tert-butoxide ("KO^tBu") was added (65 mg, 0.61 mmol, 1.0 equiv.). Immediately upon addition of KO^tBu, the tetrafluoroborate salt dissolved completely and the reaction mixture turned yellow. Complex 7, RuCl₂(=CHPh)(PCy₃)₂ (400 mg, 0.49 mmol), was added to the reaction mixture as a solution in anhydrous benzene (15 mL). The reaction mixture was heated in an oil bath at 80 °C for 80 minutes at which time ¹H NMR spectrum indicated a ratio of product (complex 2) to complex 7 of 95:5. Volatiles were removed *in vacuo* and the residue was washed under inert atmosphere with anhydrous pentane (4X 20 mL) to give pure product as a pinkish-brown microcrystalline solid (270 mg, 0.3 mmol) in 61% yield. Scheme 1 illustrates this protocol for complex 2 as well as for complexes 1 and 3.

SCHEME 1



EXAMPLE 4

The following are representative protocols for several common metathesis reactions.

RCM Reactions

- Complex 1 (42 mg, 50 μ mol, 0.05 equiv.) was added to a solution of diethyl
5 diallylmalonate (240 mg, 1 mmol, 1 equiv.) in methylene chloride (20 mL, 0.05 M). The reaction mixture was refluxed on an oil bath (45 °C) for 5 minutes at which time ^1H NMR indicated 100% conversion to cyclopent-3-ene-1,1-dicarboxylic acid diethyl ester.

Cross Metathesis Reactions:

- 10 Complex 2 (11 mg, 12 μ mol, 0.023 equiv.) was added to a mixture of 9-decen-1-yl benzoate (145 μ L, 0.525 mmol, 1 equiv.) and cis-2-buten-1,4-diol diacetate (160 μ L, 1.014 mmol, 1.93 equiv.) in methylene chloride (2.5 mL, 0.21 M). After refluxing for 3.5 hours, the mixture was purified by flash column chromatography to yield the cross metathesis product as a clear, colorless oil (140 mg, 80% yield, E:Z = 9:1).

15

ROMP Reactions with DCPD:

- Complex 1 (6.5 mg, 7.5 μ mol, 1 equiv.) in a small amount of CH_2Cl_2 (100 μ L) was added to a stirring neat dicyclopentadiene (mixture of *exo*- and *endo*-isomers) (10.0 g, 75.6 mmol, 10,000 equiv.). Within a few seconds, the reaction mixture became increasingly
20 viscous, warmed up significantly, and solidified shortly thereafter. On cooling, an odor free, nearly colorless solid was obtained.

Telechelic Synthesis:

- Complex 1 (3.1 mg, 3.7 μ mol, 1 equiv.) was added to a stirring mixture of cyclooctadiene
25 (5.00 g, 46.2 mmol, 12,500 equiv.) and 1,4-dichloro-cis-2-butene (1.16 g, 9.28 mmol, 2,500 equiv.). After 8 hours, the reaction mixture was diluted with methylene chloride (1 mL) and poured into an excess of methanol precipitating the dichloro-telechelic polybutadiene as a white solid (4.0 g, 65% yield).

30 Polymerization of 5,6-Dihydroxycyclooctene

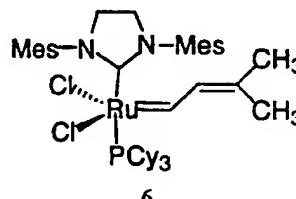
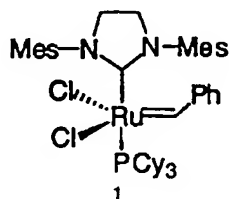
In a nitrogen filled drybox, a small vial was charged with 2 mg catalyst (1 equiv.), 150 mg 5,6-dihydroxycyclooctene (1000 equiv.), and 0.25 mL of benzene. The vial was capped tightly, removed from the drybox, and submerged in a constant temperature oil

bath set at 50 degrees. After 10 hours, a slightly yellow viscous oil formed. Upon the addition of tetrahydrofuran, a white gel separated and was found to be insoluble in all common organic solvents. Residual, unreacted monomer could be detected in the tetrahydrofuran layer by ^1H NMR.

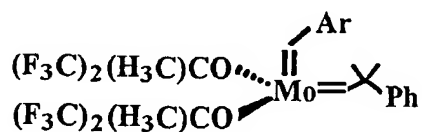
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EXAMPLE 5

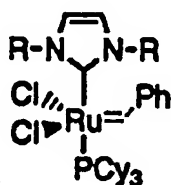
To better appreciate the advantageous properties of the inventive catalysts, the ROMP reactions of low strain cyclic olefins, cis, cis-cycloocta-1,5-diene ("COD") and cis-cyclooctene ("COE") with inventive catalysts 1 and 6



and representative prior art catalysts



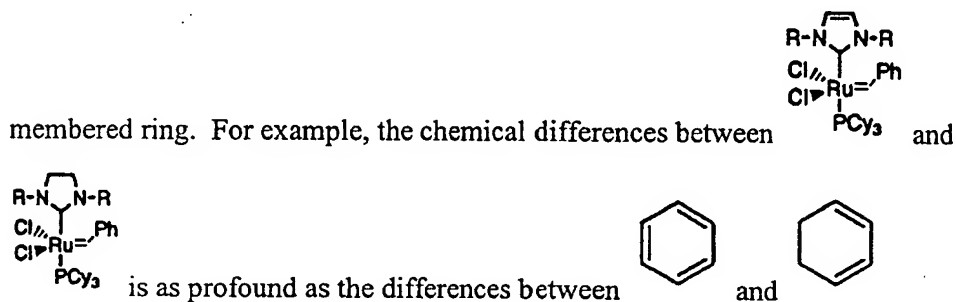
wherein Ar = C₆H₃-2,6-(tPR) ("catalyst 8")



- and wherein R = Mes ("catalyst 9") were compared. The molybdenum catalyst 8 was purchased from Strem Chemicals and recrystallized from pentane at -40 °C prior to use. For the ROMP kinetics experiments, COD, COE, and CD₂Cl₂ were distilled from CaH₂ and bubbled with argon prior to use. All polymerizations were performed under an atmosphere of nitrogen.
- The ROMP of COD and COE were catalyzed with the respective catalysts and the percent monomer converted to polymer was followed over time using ^1H NMR spectroscopy. As shown by Figures 1 and 2, the rate of polymerization at 20°C using catalyst 1 was significantly higher than the molybdenum catalyst 8. As illustrated by Figure 3, the rate

of polymerization at 55°C using catalysts 6 and 9 were also higher than for the molybdenum catalyst 8. Because the propagating species resulting from catalysts 1 and 6 are the same, the observed difference in polymerization rates between them is believed to be due to the initiation rate. The bulkier benzylidene is believed to facilitate phosphine dissociation thereby enhancing initiation to a greater extent than the dimethylvinyl carbene counterpart. Previous studies have shown that alkylidene electronics have a relatively small influence on the initiation rate.

Although imidazole-based catalysts such as catalyst 9 and the imidazoline-based catalyst of the present invention may appear structurally similar, they possess vastly different chemical properties due to the differences in their electronic character of the five



15

EXAMPLE 6

The catalysts of the present invention are capable of polymerizing a variety of low strain cyclic olefins including cyclooctadiene, cyclooctene, and several functionalized and sterically hindered derivatives with extremely low catalyst loadings (up to
 5 monomer/catalysts = 100,000). Representative results are shown by Table 3.

Table 3: ROMP of various low strain cyclic olefins

Monomer	Monomer to Catalyst Ratio	Temp. (°C)	Time	Yield (%)	M _n (PDI) ^a	% Trans ^b
1,5 cyclooctadiene	100,000	55	30 min	85	112,400 (2.3)	70
	10,000	25	24 h	85	92,900 (2.5)	85
	25,000	55	24 h	89	10,700 (2.1)	90
cyclooctene	100,000	55	5 min	e	e	f
	10,000	25	30 min	e	e	f
	25,000 ^c	55	24 h	75	2200 (1.6)	85
1-hydroxy 4-cyclooctene	100,000	55	5 min	e	e	f
	10,000	25	30 min	e	e	f
	25,000 ^d	55	24 h	85	2600 (2.3)	85
1-acetoxy-4-cyclooctene	10,000	55	5 min	50	103,900 (2.8)	85
	1000	25	1 h	60	79,300 (3.2)	90
5-methylcyclopentene	1000	25	24 h	50	23,000 (2.5)	50
cyclopentene	1000	25	24 h	52	9000 (3.5)	90

^a Determined by CH₂Cl₂ or THF GPC and results are reported relative to poly(styrene) standards; ^b Percent trans olefin in the polymer backbone as determined by ¹H and ¹³C NMR analysis; ^c 1,4-diacetoxy-cis-2-butene was included as a chain transfer agent ("CTA") wherein the Monomer/CTA = 80; ^d Monomer/CTA = 10, [Monomer]₀ = 4.5 M in C₂H₄Cl₂; ^e Polymer was insoluble; ^f Not determined.

Elevated temperatures (55 °C) generally increased the yields of polymer while reducing
 15 reaction times. The inclusion of acyclic olefins which act as chain transfer agents controlled the molecular weights. The addition of CTAs is desirable when insoluble polymers are obtained by ring-opening monomers such as COE in bulk. Polymers possessing alcohols or acetic ester along their backbone could also be prepared using functionalized monomers such as 5-hydroxy- or 5-acetoxy-cyclooctene. The functional
 20 groups on these polymers could easily be derivatized to form graft copolymers or side-chain liquid crystalline polymers. In general, ¹H NMR spectroscopy indicated a predominantly (70-90%) trans-olefin microstructure in these polymers. As expected for

an equilibrium controlled polymerization where chain transfer occurs, longer polymerization times resulted in higher trans-olefin values.

5

EXAMPLE 7

A highly strained monomer, *exo,exo*-5,6-bis(methoxymethyl)-7-oxabicyclo[2.2.1]hept-2-ene, was polymerized via ROMP reaction using catalyst 1 in the presence of 1,4-diacetoxy-2-butene as a chain transfer agent. The reaction was conducted in C₂H₄Cl₂ at 55 °C for 24 hours and resulted in a bis-(acetoxy) end-terminated polymer in 80% yield (M_n = 6300, PDI 2.0). This result is particularly notable since telechelic polymers composed of highly strained monomers are relatively difficult to obtain using other methods. For example, a metathesis degradation approach using a tungsten analog of catalyst 8 has been used to prepare telechelic poly(oxanorbornene)s and poly(norbornene)s. However, only certain telechelic polymers are amenable to this approach since the limited ability of the tungsten catalyst to tolerate functional groups imposes a severe restriction on the range of chain transfer agents that may be used. Alternatively, a "pulsed addition" approach has been used with catalysts 7 and 8. However, because monomer and/or CTA must be added in a carefully timed manner, this approach is relatively difficult to perform and is not readily amenable to industrial applications.

20

EXAMPLE 8

1,5-dimethyl-1,5-cyclooctadiene, a sterically hindered, low strain, di-substituted cyclic olefin was polymerized using catalyst 1. The 1,5-dimethyl-1,5-cyclooctadiene used in this study contained 1,6-dimethyl-1,5-cyclooctadiene (20%) as an inseparable mixture. This ROMP reaction was performed at 55 °C with monomer/catalyst ratio of 1000 and resulted in a 90% yield of poly(isoprene) having a M_n of 10,000 and a PDI of 2.3. To the best of our knowledge, this example represents the first ROMP of this monomer. Subsequent hydrogenation using p-toluenesulfonylhydrazide as a hydrogen source afforded an ethylene-propylene copolymer in quantitative yield (as determined by NMR analysis). Previously, a six step synthesis was necessary to obtain a similar copolymer via a metathetical route.

30

The resulting ethylene-propylene copolymer was not "perfectly" alternating because of the impurity in the 1,5-dimethyl-1-5-cyclooctadiene starting material. However, since trisubstituted alkylidenes were not observed as a side product, poly(isoprene) product
5 having perfectly alternating head to tail microstructure would have likely been formed if a higher grade of 1,5-dimethyl-1-5-cyclooctadiene were used. As a result, practice of the present invention could result in a perfectly alternating ethylene-propylene product.

EXAMPLE 9

10 2-methyl-1-undecene (110 μ L, 0.5 mmol) and 5-hexenyl-1-acetate (170 μ L, 1.0 mmol) were simultaneously added *via* syringe to a stirring solution of complex 1 (20 mg, 0.024 mmol, 4.8 mol %) in CH_2Cl_2 (2.5 mL). The flask was fitted with a condenser and refluxed under nitrogen for 12 hours. The reaction mixture was then reduced in volume to 0.5 ml and purified directly on a silica gel column (2x10 cm), eluting with 9:1
15 hexane:ethyl acetate. A clear oil was obtained (83 mg, 60% yield, 2.3:1 *trans/cis* as determined by relative intensity of alkene ^{13}C peaks at 125.0 and 124.2 ppm). ^1H NMR (300 MHz, CDCl_3 , ppm): 5.08 (1H, t, $J = 2.0$ Hz), 4.04 (2H, t, $J = 6.0$ Hz), 2.03 (3H, obs s), 2.01-1.91 (2H, m), 1.69-1.59 (2H, m), 1.56 (3H, obs s), 1.47-1.05 (16H, broad m), 1.05-0.84 (3H, t, $J = 6.8$ Hz) ^{13}C NMR (75 MHz, CDCl_3 , ppm): 171.7, 136.7, 136.4,
20 125.0, 124.2, 123.3, 65.1, 40.3, 32.5, 32.3, 30.2, 29.9, 28.8, 28.6, 28.5, 28.0, 26.7, 23.2, 21.5, 16.4, 14.7. $R_f = 0.35$ (9:1 hexane:ethyl acetate); HRMS (EI) calcd for $\text{C}_{18}\text{H}_{34}\text{O}_2$ $[\text{M}]^+$ 282.2559, found 282.2556.

25

EXAMPLE 10

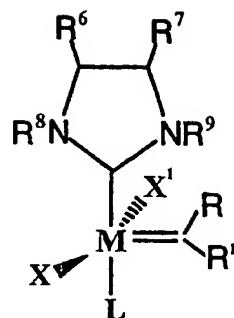
9-Decen-1(*tert*-butyldimethylsilane)-yl (330 μ L, 1.0 mmol) and Methyl methacrylate (55 μ L, 0.51 mmol) were added simultaneously *via* syringe to a stirring solution of complex 1 (21 mg, 0.026 mmol, 5.2 mol %) in CH_2Cl_2 (2.5 ml). The flask was fitted with a condenser and refluxed under nitrogen for 12 hours. The reaction mixture was then
30 reduced in volume to 0.5 ml and purified directly on a silica gel column (2x10 cm), eluting with 9:1 hexane:ethyl acetate. A viscous oil was obtained (110 mg, 62% yield, only *trans* isomer detected in ^1H and ^{13}C NMR spectra). ^1H NMR (300 MHz, CDCl_3 ,

ppm): δ 6.75 (1H, m), 3.71 (3H, s), 3.57 (2H, t, $J = 6.3$ Hz), 2.14 (2H, m), 1.81 (3H, app s), 1.50 – 1.05 (12H, broad m), 0.87 (9H, s), 0.02 (6H, s). ^{13}C NMR (75 MHz, CDCl_3 , ppm): δ 169.2, 143.2, 128.0, 63.8, 52.1, 33.4, 30.0, 29.8, 29.2, 29.1, 26.5, 26.3, 18.9, 12.9. $R_f = 0.81$ (9:1 hexane:ethyl acetate); HRMS (EI) calcd for $\text{C}_{19}\text{H}_{38}\text{O}_3\text{Si}$ $[\text{M} + \text{H}]^+$

- 5 343.2668, found 343.2677. Elemental analysis calcd: C: 66.61, H: 11.18; found: C: 66.47, H: 11.03.

What is claimed is:

1. A compound of the formula



wherein:

M is ruthenium or osmium;

X and X' are each independently an anionic ligand;

L is a neutral electron donor ligand; and,

R, R¹, R⁶, R⁷, R⁸, and R⁹ are each independently hydrogen or a substituent selected from the group consisting of C₁-C₂₀ alkyl, C₂-C₂₀ alkenyl, C₂-C₂₀ alkynyl, aryl, C₁-C₂₀ carboxylate, C₁-C₂₀ alkoxy, C₂-C₂₀ alkenyloxy, C₂-C₂₀ alkynyloxy, aryloxy, C₂-C₂₀ alkoxycarbonyl, C₁-C₂₀ alkylthiol, aryl thiol, C₁-C₂₀ alkylsulfonyl and C₁-C₂₀ alkylsulfinyl, the substituent optionally substituted with one or more moieties selected from the group consisting of C₁-C₁₀ alkyl, C₁-C₁₀ alkoxy, aryl, and a functional group selected from the group consisting of hydroxyl, thiol, thioether, ketone, aldehyde, ester, ether, amine, imine, amide, nitro, carboxylic acid, disulfide, carbonate, isocyanate, carbodiimide, carboalkoxy, carbamate, and halogen.

2. The compound as in claim 1 wherein:

M is ruthenium;

L and L¹ are each independently selected from the group consisting of phosphine, sulfonated phosphine, phosphite, phosphinite, phosphonite, arsine, stibine, ether, amine, amide, imine, sulfoxide, carboxyl, nitrosyl, pyridine, and thioether; and,

X and X' are each independently hydrogen, halide, or a substituent selected from the group consisting of C₁-C₂₀ alkyl, aryl, C₁-C₂₀ alkoxide, aryloxide, C₃-C₂₀ alkyldiketonate, aryldiketonate, C₁-C₂₀ carboxylate, arylsulfonate, C₁-C₂₀ alkylsulfonate,

C₁-C₂₀ alkylthiol, aryl thiol, C₁-C₂₀ alkylsulfonyl, and C₁-C₂₀ alkylsulfinyl, the substituent optionally substituted with one or more moieties selected from the group consisting of C₁-C₁₀ alkyl, C₁-C₁₀ alkoxy, aryl and halide.

3. The compound as in claim 1 wherein:

M is ruthenium;

X and X¹ are each independently selected from the group consisting of halide, CF₃CO₂, CH₃CO₂, CFH₂CO₂, (CH₃)₃CO, (CF₃)₂(CH₃)CO, (CF₃)(CH₃)₂CO, PhO, MeO, EtO, tosylate, mesylate, and trifluoromethanesulfonate;

L is a phosphine of the formula PR³R⁴R⁵, where R³, R⁴, and R⁵ are each independently aryl, C₁-C₁₀ alkyl, or cycloalkyl;

R is hydrogen; and,

R¹ is phenyl or vinyl, optionally substituted with one or more moieties selected from the group consisting of C₁-C₅ alkyl, C₁-C₅ alkoxy, phenyl, and a functional group selected from the group consisting of hydroxyl, thiol, thioether, ketone, aldehyde, ester, ether, amine, imine, amide, nitro, carboxylic acid, disulfide, carbonate, isocyanate, carbodiimide, carboalkoxy, carbamate, and halogen.

4. The compound as in claim 3 wherein

X and X¹ are each chloride;

L is selected from the group consisting of -P(cyclohexyl)₃, -P(cyclopentyl)₃, -P(isopropyl)₃, and -P(phenyl)₃; and,

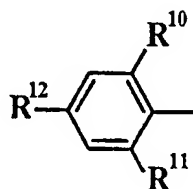
R¹ is phenyl or -C=C(CH₃)₂;

5. The compound as in claim 4 wherein R⁶ and R⁷ together form a cycloalkyl or an aryl.

6. The compound as in claim 4 wherein R⁶ and R⁷ together form a cyclopentyl or a cyclohexyl moiety.

7. The compound as in claim 4 wherein R⁶ and R⁷ are the same and are hydrogen or phenyl.

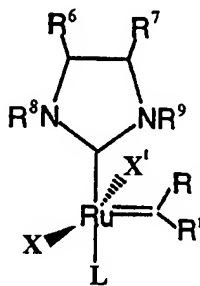
8. The compound as in claim 4 wherein R^8 and R^9 are each independently a substituted or unsubstituted aryl.
9. The compound as in claim 4 wherein R^8 and R^9 are the same and are phenyl.
10. The compound as in claim 4 wherein R^8 and R^9 are each independently of the formula



wherein

R^{10} , R^{11} , and R^{12} are each independently hydrogen, C_1 - C_{10} alkyl, C_1 - C_{10} alkoxy, aryl, or a functional group selected from hydroxyl, thiol, thioether, ketone, aldehyde, ester, ether, amine, imine, amide, nitro, carboxylic acid, disulfide, carbonate, isocyanate, carbodiimide, carboalkoxy, carbamate, and halogen.

11. The compound as in claim 10 wherein R^{10} , R^{11} , and R^{12} are each independently hydrogen, methyl or isopropyl.
12. A compound of the formula



wherein:

X and X' are each chloride;

L is selected from the group consisting of $-P(\text{cyclohexyl})_3$, $-P(\text{cyclopentyl})_3$, $-P(\text{isopropyl})_3$, and $-P(\text{phenyl})_3$;

R is hydrogen;

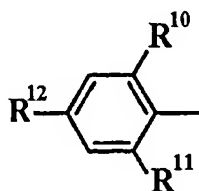
R^1 is phenyl or vinyl, optionally substituted with one or more moieties selected from the group consisting of C_1 - C_5 alkyl, C_1 - C_5 alkoxy, phenyl, and a functional group selected from the group consisting of hydroxyl, thiol, thioether, ketone, aldehyde, ester, ether, amine, imine, amide, nitro, carboxylic acid, disulfide, carbonate, isocyanate, carbodiimide, carboalkoxy, carbamate, and halogen;

R^6 and R^7 are each independently hydrogen, phenyl, or together form a cycloalkyl or an aryl optionally substituted with one or more moieties selected from the group consisting of C_1 - C_{10} alkyl, C_1 - C_{10} alkoxy, aryl, and a functional group selected from the group consisting of hydroxyl, thiol, thioether, ketone, aldehyde, ester, ether, amine, imine, amide, nitro, carboxylic acid, disulfide, carbonate, isocyanate, carbodiimide, carboalkoxy, carbamate, and halogen; and

R^8 and R^9 are each is independently C_1 - C_{10} alkyl or aryl optionally substituted with C_1 - C_5 alkyl, C_1 - C_5 alkoxy, aryl, and a functional group selected from the group consisting of hydroxyl, thiol, thioether, ketone, aldehyde, ester, ether, amine, imine, amide, nitro, carboxylic acid, disulfide, carbonate, isocyanate, carbodiimide, carboalkoxy, carbamate, and halogen.

13. The compound as in claim 12 wherein R^8 and R^9 are each is independently a cycloalkyl or a phenyl optionally substituted with C_1 - C_5 alkyl, C_1 - C_5 alkoxy, or halogen.

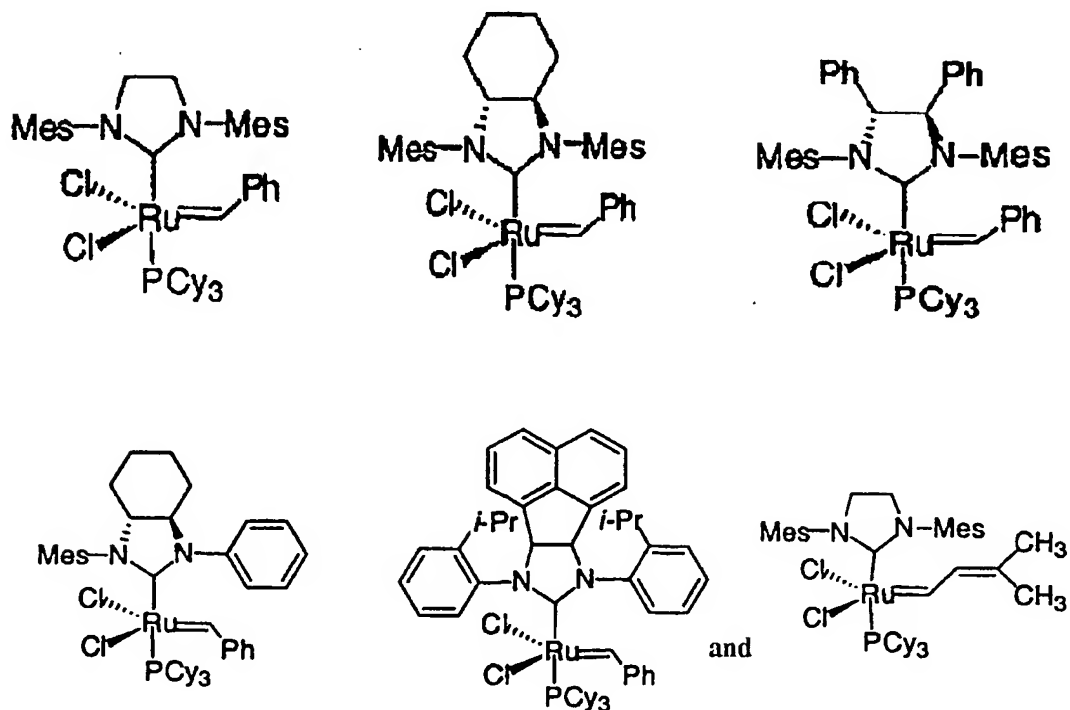
14. The compound as in claim 12 wherein R^8 and R^9 are each independently of the formula



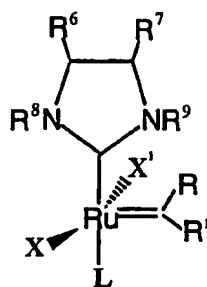
wherein

R^{10} , R^{11} , and R^{12} are each independently hydrogen, C_1 - C_{10} alkyl, C_1 - C_{10} alkoxy, aryl, or a functional group selected from hydroxyl, thiol, thioether, ketone, aldehyde, ester, ether, amine, imine, amide, nitro, carboxylic acid, disulfide, carbonate, isocyanate, carbodiimide, carboalkoxy, carbamate, and halogen.

15. The compound as in claim 14 wherein R^{10} , R^{11} , and R^{12} are the same and are each methyl.
16. The compound as in claim 12 selected from the group consisting of



17. A compound of the formula



wherein:

X and X^1 are each chloride;

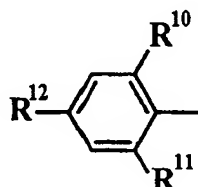
L is selected from the group consisting of $-P(\text{cyclohexyl})_3$, $-P(\text{cyclopentyl})_3$, $-P(\text{isopropyl})_3$, and $-P(\text{phenyl})_3$;

R is hydrogen;

R¹ is phenyl or -C=C(CH₃)₂;

R⁶ and R⁷ are each independently hydrogen, phenyl, or together form a cyclopentyl or cyclohexyl; and

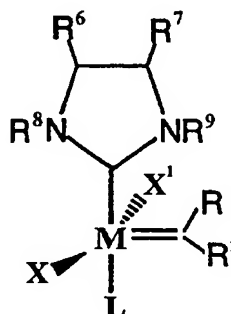
R⁸ and R⁹ are each is independently of the formula



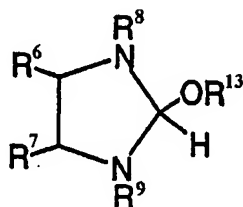
wherein

R¹⁰, R¹¹, and R¹² are each independently hydrogen, methyl, ethyl, propyl, isopropyl, hydroxyl, and halogen.

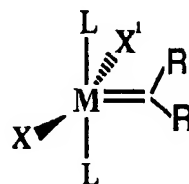
18. A method for making a compound of the formula



comprising contacting



with



wherein:

M is ruthenium or osmium;

X and X¹ are each independently an anionic ligand;

L is a neutral electron donor ligand;

R, R¹, R⁶, R⁷, R⁸, and R⁹ are each independently hydrogen or a substituent selected from the group consisting of C₁-C₂₀ alkyl, C₂-C₂₀ alkenyl, C₂-C₂₀ alkynyl, aryl, C₁-C₂₀

carboxylate, C₁-C₂₀ alkoxy, C₂-C₂₀ alkenyloxy, C₂-C₂₀ alkynyloxy, aryloxy, C₂-C₂₀ alkoxycarbonyl, C₁-C₂₀ alkylthiol, aryl thiol, C₁-C₂₀ alkylsulfonyl and C₁-C₂₀ alkylsulfinyl, the substituent optionally substituted with one or more moieties selected from the group consisting of C₁-C₁₀ alkyl, C₁-C₁₀ alkoxy, aryl, and a functional group selected from the group consisting of hydroxyl, thiol, thioether, ketone, aldehyde, ester, ether, amine, imine, amide, nitro, carboxylic acid, disulfide, carbonate, isocyanate, carbodiimide, carboalkoxy, carbamate, and halogen; and,

R¹³ is C₁-C₂₀ alkyl or aryl.

19. The method as in claim 18 wherein

M is ruthenium;

X and X¹ are each chloride;

L is selected from the group consisting of -P(cyclohexyl)₃, -P(cyclopentyl)₃, -P(isopropyl)₃, and -P(phenyl)₃;

R is hydrogen;

R¹ is phenyl or -C=C(CH₃)₂;

R⁶ and R⁷ are each independently hydrogen, phenyl, or together form a cyclophenyl or cyclohexyl; and,

R⁸ and R⁹ are each independently a substituted or unsubstituted aryl.

20. The method as in claim 19 wherein R¹³ is t-butyl.

21. The method as in claim 18 wherein

M is ruthenium;

X and X¹ are each chloride;

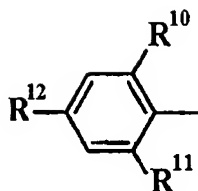
L is selected from the group consisting of -P(cyclohexyl)₃, -P(cyclopentyl)₃, -P(isopropyl)₃, and -P(phenyl)₃;

R is hydrogen;

R¹ is phenyl or -C=C(CH₃)₂;

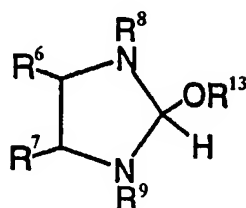
R⁶ and R⁷ together form a cycloalkyl group; and

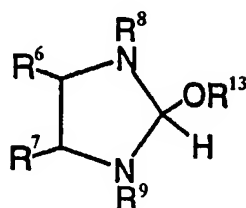
R⁸ and R⁹ are the same and are each of the formula



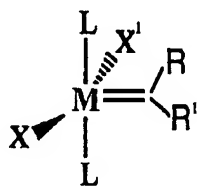
wherein

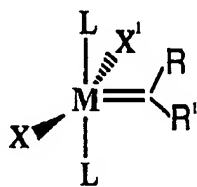
R¹⁰, R¹¹, and R¹² are each independently hydrogen, methyl, ethyl, propyl, isopropyl, hydroxyl, and halogen.



22. The method as in claim 21 wherein  is optically active.

23. A method for making a metathesis catalyst comprising contacting a compound of



the formula  with an imidazolidine whereby the imidazolidine replaces one of the L ligands wherein:

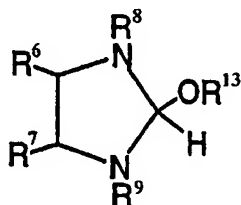
M is ruthenium or osmium;

X and X¹ are each independently an anionic ligand;

L is a neutral electron donor ligand; and,

R and R¹ are each independently hydrogen or a substituent selected from the group consisting of C₁-C₂₀ alkyl, C₂-C₂₀ alkenyl, C₂-C₂₀ alkynyl, aryl, C₁-C₂₀ carboxylate, C₁-C₂₀ alkoxy, C₂-C₂₀ alkenyloxy, C₂-C₂₀ alkynyloxy, aryloxy, C₂-C₂₀ alkoxycarbonyl, C₁-C₂₀ alkylthiol, aryl thiol, C₁-C₂₀ alkylsulfonyl and C₁-C₂₀ alkylsulfinyl, the substituent optionally substituted with one or more moieties selected from the group consisting of C₁-C₁₀ alkyl, C₁-C₁₀ alkoxy, aryl, and a functional group selected from the group consisting of hydroxyl, thiol, thioether, ketone, aldehyde, ester, ether, amine, imine, amide, nitro, carboxylic acid, disulfide, carbonate, isocyanate, carbodiimide, carboalkoxy, carbamate, and halogen.

24. The method as in claim 23 wherein the imidazolidine is formed by contacting a secondary diamine with ammonium tetrafluoroborate to form an imidazolium salt; and contacting the imidazolium salt with an alkoxide to form the imidazolidine.
25. The method as in claim 24 wherein the secondary diamine is formed by contacting a diketone with an amine to form a diimine and hydrogenating the diimine to form the secondary di-amine;
26. The method as in claim 24 wherein the alkoxide is t-butoxide.
27. The method as in claim 24 wherein the imidazolidine is of the formula



wherein

R^6 , R^7 , R^8 , and R^9 are each independently hydrogen or a substituent selected from the group consisting of C_1 - C_{20} alkyl, C_2 - C_{20} alkenyl, C_2 - C_{20} alkynyl, aryl, C_1 - C_{20} carboxylate, C_1 - C_{20} alkoxy, C_2 - C_{20} alkenyloxy, C_2 - C_{20} alkynyloxy, aryloxy, C_2 - C_{20} alkoxy carbonyl, C_1 - C_{20} alkylthiol, aryl thiol, C_1 - C_{20} alkylsulfonyl and C_1 - C_{20} alkylsulfinyl, the substituent optionally substituted with one or more moieties selected from the group consisting of C_1 - C_{10} alkyl, C_1 - C_{10} alkoxy, aryl, and a functional group selected from the group consisting of hydroxyl, thiol, thioether, ketone, aldehyde, ester, ether, amine, imine, amide, nitro, carboxylic acid, disulfide, carbonate, isocyanate, carbodiimide, carboalkoxy, carbamate, and halogen; and,

R^{13} is C_1 - C_{20} alkyl or aryl.

28. The method as in claim 27 wherein
M is ruthenium;
X and X^1 are each chloride;

L is selected from the group consisting of -P(cyclohexyl)₃, -P(cyclopentyl)₃, -P(isopropyl)₃, and -P(phenyl)₃;

R is hydrogen; and

R¹ is phenyl or vinyl, optionally substituted with one or more moieties selected from the group consisting of C₁-C₅ alkyl, C₁-C₅ alkoxy, phenyl, and a functional group selected from the group consisting of hydroxyl, thiol, thioether, ketone, aldehyde, ester, ether, amine, imine, amide, nitro, carboxylic acid, disulfide, carbonate, isocyanate, carbodiimide, carboalkoxy, carbamate, and halogen.

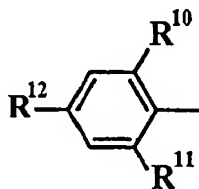
29. The method as in claim 28 wherein R¹ is phenyl or -C=C(CH₃)₂ and R¹³ is t-butoxide.

30. The method as in claim 28 wherein

R⁶ and R⁷ are each independently hydrogen, phenyl, or together form a cycloalkyl or an aryl optionally substituted with one or more moieties selected from the group consisting of C₁-C₁₀ alkyl, C₁-C₁₀ alkoxy, aryl, and a functional group selected from the group consisting of hydroxyl, thiol, thioether, ketone, aldehyde, ester, ether, amine, imine, amide, nitro, carboxylic acid, disulfide, carbonate, isocyanate, carbodiimide, carboalkoxy, carbamate, and halogen; and

R⁸ and R⁹ are each independently either substituted or unsubstituted aryl.

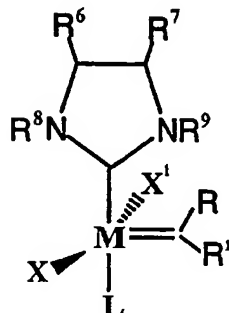
31. The method as in claim 30 wherein R⁸ and R⁹ are each is independently of the formula



wherein

R¹⁰, R¹¹, and R¹² are each independently hydrogen, methyl, ethyl, propyl, isopropyl, hydroxyl, and halogen.

32. A method for performing a metathesis reaction comprising contacting an olefin with a compound of the formula



wherein:

M is ruthenium or osmium;

X and X¹ are each independently an anionic ligand;

L is a neutral electron donor ligand; and,

R, R¹, R⁶, R⁷, R⁸, and R⁹ are each independently hydrogen or a substituent selected from the group consisting of C₁-C₂₀ alkyl, C₂-C₂₀ alkenyl, C₂-C₂₀ alkynyl, aryl, C₁-C₂₀ carboxylate, C₁-C₂₀ alkoxy, C₂-C₂₀ alkenyloxy, C₂-C₂₀ alkynyloxy, aryloxy, C₂-C₂₀ alkoxycarbonyl, C₁-C₂₀ alkylthiol, aryl thiol, C₁-C₂₀ alkylsulfonyl and C₁-C₂₀ alkylsulfinyl, the substituent optionally substituted with one or more moieties selected from the group consisting of C₁-C₁₀ alkyl, C₁-C₁₀ alkoxy, aryl, and a functional group selected from the group consisting of hydroxyl, thiol, thioether, ketone, aldehyde, ester, ether, amine, imine, amide, nitro, carboxylic acid, disulfide, carbonate, isocyanate, carbodiimide, carboalkoxy, carbamate, and halogen.

33. The method as in claim 32 wherein:

M is ruthenium;

X and X¹ are each chloride;

L is selected from the group consisting of -P(cyclohexyl)₃, -P(cyclopentyl)₃, -P(isopropyl)₃, and -P(phenyl)₃;

R is hydrogen;

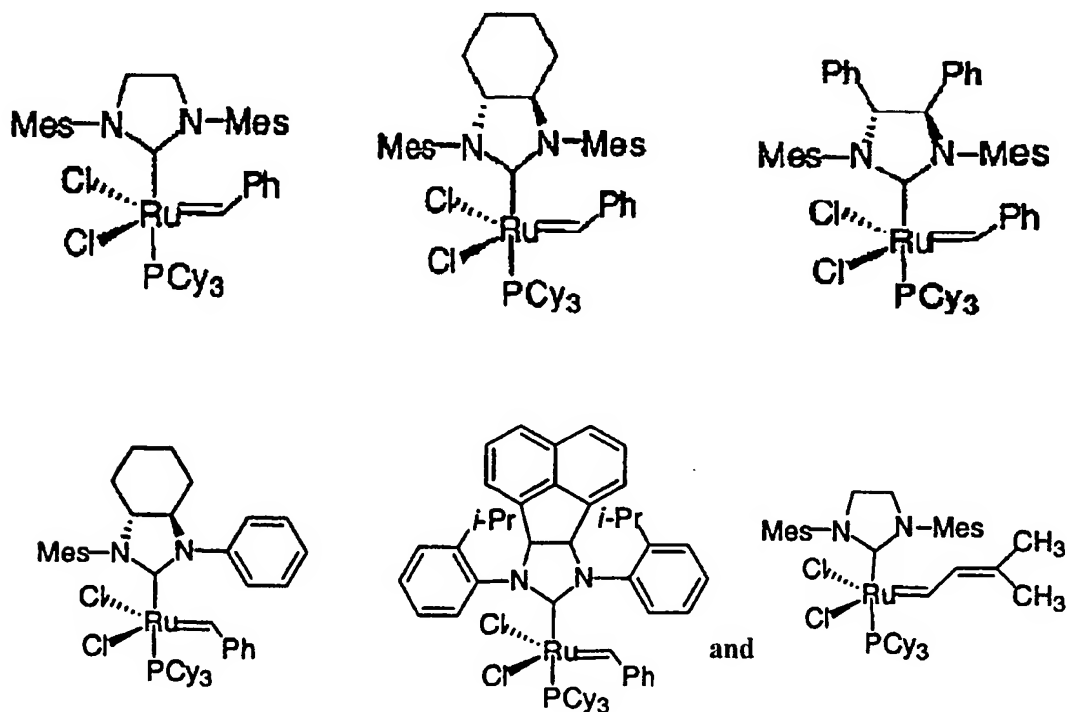
R¹ is phenyl or vinyl, optionally substituted with one or more moieties selected from the group consisting of C₁-C₅ alkyl, C₁-C₅ alkoxy, phenyl, and a functional group selected from the group consisting of hydroxyl, thiol, thioether, ketone, aldehyde, ester,

ether, amine, imine, amide, nitro, carboxylic acid, disulfide, carbonate, isocyanate, carbodiimide, carboalkoxy, carbamate, and halogen;

R^6 and R^7 are each independently hydrogen, phenyl, or together form a cycloalkyl or an aryl optionally substituted with one or more moieties selected from the group consisting of C_1 - C_{10} alkyl, C_1 - C_{10} alkoxy, aryl, and a functional group selected from the group consisting of hydroxyl, thiol, thioether, ketone, aldehyde, ester, ether, amine, imine, amide, nitro, carboxylic acid, disulfide, carbonate, isocyanate, carbodiimide, carboalkoxy, carbamate, and halogen; and

R^8 and R^9 are each is independently C_1 - C_{10} alkyl or aryl optionally substituted with C_1 - C_5 alkyl, C_1 - C_5 alkoxy, aryl, and a functional group selected from the group consisting of hydroxyl, thiol, thioether, ketone, aldehyde, ester, ether, amine, imine, amide, nitro, carboxylic acid, disulfide, carbonate, isocyanate, carbodiimide, carboalkoxy, carbamate, and halogen.

34. The method as in claim 32 wherein the compound is selected from the group consisting of



35. The method as in claim 33 wherein the olefin is a cyclic olefin.

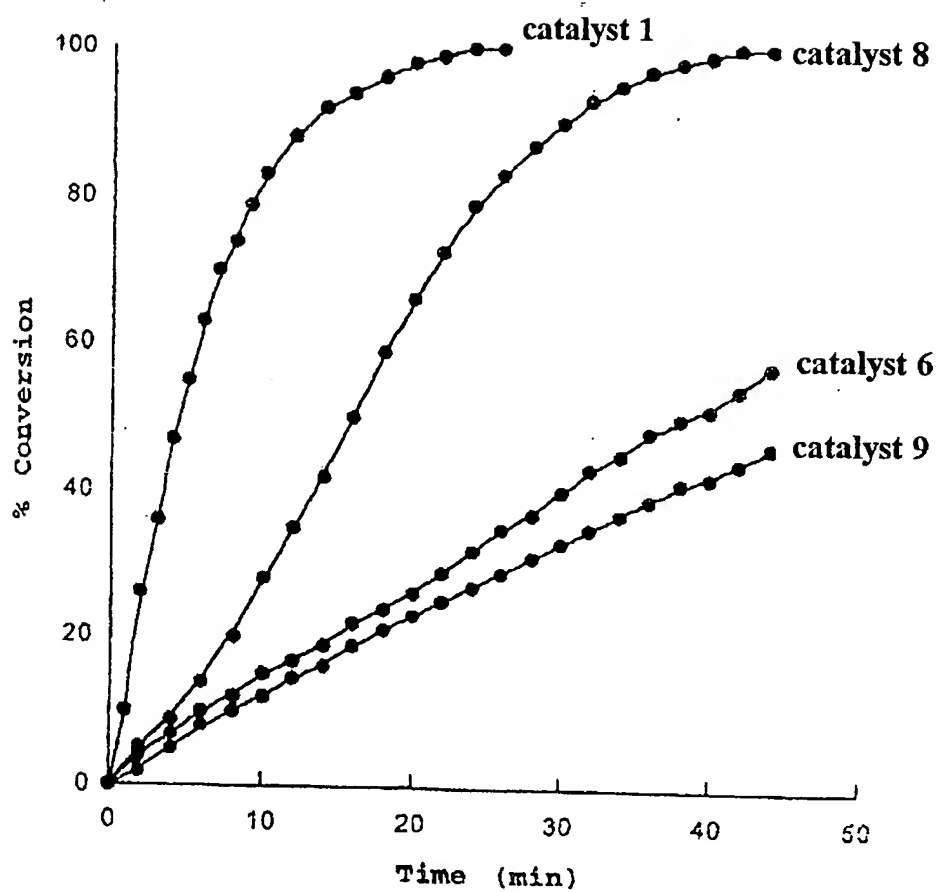


Figure 1

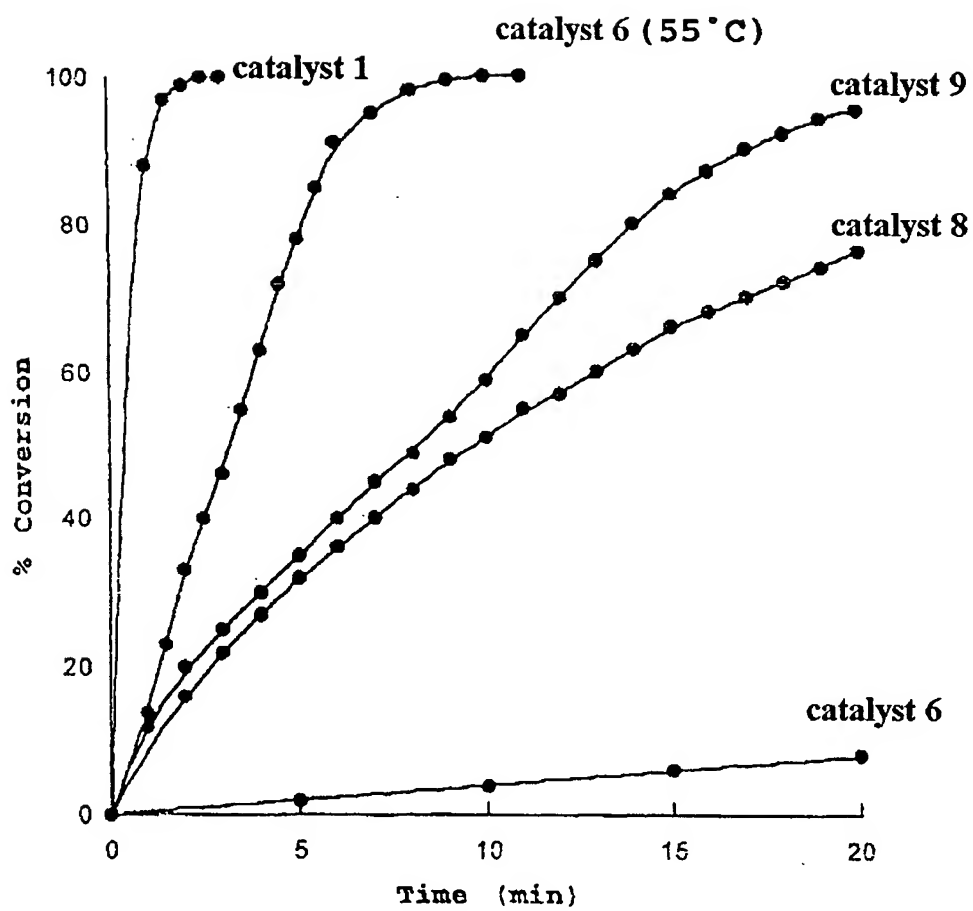
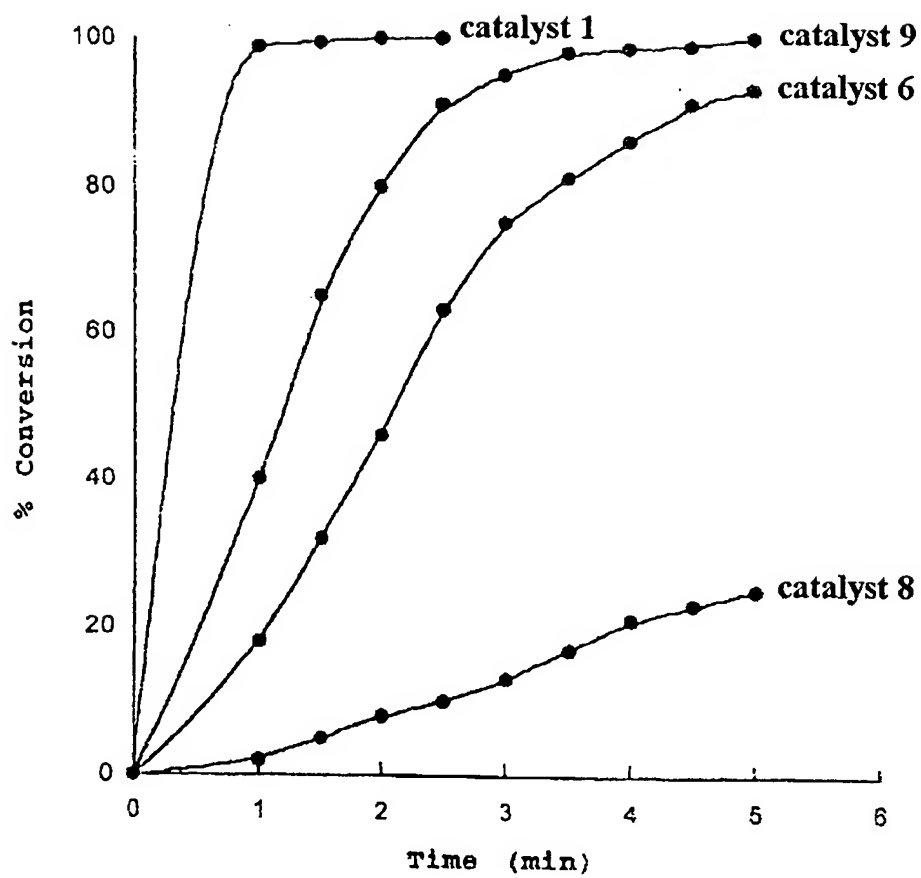


Figure 2

**Figure 3**

(19) World Intellectual Property Organization
International Bureau



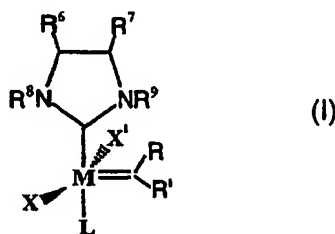
(43) International Publication Date
30 November 2000 (30.11.2000)

PCT

(10) International Publication Number
WO 00/71554 A3

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- (21) International Application Number: PCT/US00/14048
- (22) International Filing Date: 22 May 2000 (22.05.2000)
- (25) Filing Language: English
- (26) Publication Language: English
- (30) Priority Data:
60/135,493 24 May 1999 (24.05.1999) US
60/142,853 7 July 1999 (07.07.1999) US
- (71) Applicant (for all designated States except US): CALIFORNIA INSTITUTE OF TECHNOLOGY [US/US]; 1200 East California Boulevard, Pasadena, Ca 91125 (US).
- (72) Inventors; and
- (75) Inventors/Applicants (for US only): GRUBBS, Robert, H. [US/US]; 1700 Spruce Street, South Pasadena, CA 91030 (US). SCHOLL, Matthias [DE/US]; 122-A E. Foothill Boulevard, Arcadia, CA 91006 (US).
- (74) Agents: GARDE, Tanuja, V. et al.; Pillsbury Madison & Sutro LLP, 50 Fremont Street, San Francisco, CA 94105 (US).
- (81) Designated States (national): AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CR, CU, CZ, DE, DK, DM, DZ, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, TZ, UA, UG, US, UZ, VN, YU, ZA, ZW.
- (84) Designated States (regional): ARIPO patent (GH, GM, KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG).
- Published:
— With international search report.
- (88) Date of publication of the international search report:
5 July 2001
- For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

(54) Title: IMIDAZOLIDINE-BASED METAL CARBENE METATHESIS CATALYSTS



(57) Abstract: The present invention relates to novel metathesis catalysts with an imidazolidine-based ligand and to methods for making and using the same. The inventive catalysts are of formula (I) wherein: M is ruthenium or osmium; X and X' are each independently an anionic ligand; L is a neutral electron donor ligand; and, R, R¹, R⁶, R⁷, R⁸ and R⁹ are each independently hydrogen or a substituent selected from the group consisting of C₁-C₂₀ alkyl, C₂-C₂₀ alkenyl, C₂-C₂₀ alkynyl, aryl, C₁-C₂₀ carboxylate, C₁-C₂₀ alkoxy, C₂-C₂₀ alkenyloxy, C₂-C₂₀ alkynyloxy, aryloxy, C₂-C₂₀ alkoxy-carbonyl, C₁-C₂₀ alkylthiol, aryl thiol, C₁-C₂₀ alkylsulfonyl and C₁-C₂₀ alkylsulfinyl, the substituent optionally substituted with one or more moieties selected from the group consisting of C₁-C₁₀ alkyl, C₁-C₁₀ alkoxy, aryl, and a functional group selected from the group consisting of hydroxyl, thiol thioether, ketone, aldehyde, ester, ether, amine, imine, amide, nitro, carboxylic acid, disulfide, carbonate, isocyanate, carbodiimide, carboalkoxy, carbamate, and halogen. The inclusion of an imidazolidine ligand to the previously described ruthenium or osmium catalysts has been found to dramatically improve the properties of these complexes. The inventive catalysts maintains the functional group tolerance of previously described ruthenium complexes while having enhanced metathesis activity that compares favorably to prior art tungsten and molybdenum systems.

INTERNATIONAL SEARCH REPORT

Inta. .onal Application No:
PCT/US 00/14048

A. CLASSIFICATION OF SUBJECT MATTER
C07D233/02,C07D235/02,B01J31/22

According to International Patent Classification (IPC) or to both national classification and IPC⁷

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
C07D,B01J

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
P, X	CHEMICAL ABSTRACTS, vol. 131, no. 21, 22 November 1999 Columbus, Ohio, US; abstract no. 285987k, SCHOLL, M. et al.: 'Synthesis and Activity of a New Generation of Ruthenium-Based Olefin Metathesis Catalysts Coordinated with 1,3-Dimesityl-4,5- -dihydroimidazol-2-ylidene Ligands' column 1; & Org. Lett., vol. 1, no. 6, 1999, pages 953-956, abstract. --	1-35

☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

* Special categories of cited documents:

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"E" earlier document but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

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"&" document member of the same patent family

Date of the actual completion of the international search

18 August 2000

Date of mailing of the international search report

24.01.2001

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INTERNATIONAL SEARCH REPORT

International Application No.

- 2 -

PCT/US 00/14048

C. (Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT		
Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
P, X	CHEMICAL ABSTRACTS, vol. 131, no. 22, 29 November 1999 Columbus, Ohio, US; abstract no. 299544a, WESKAMP, T.: 'Highly active ruthenium catalysts for olefin metathesis: the synergy of N-Heterocyclic carbenes and coordinatively labile ligands' page 567; column 1; & Angew. Chem., Int. Ed., vol. 38, no. 16, 1999, pages 2416-2419, abstract. ---	1-35
A	CHEMICAL ABSTRACTS, vol. 130, no. 4, 25 January 1999 Columbus, Ohio, US; abstract no. 38522n, WESKAMP, T. et al.: 'A novel class of ruthenium catalysts for olefin metathesis' page 709; column 2; & Angew. Chem., Int. Ed., vol. 37, no. 18, 1998, pages 2490-2493, abstract. --	1-35
A	US 5831108 A (GRUBBS et al.) 03 November 1998, the whole document. ----	1-35

ANHANG

Zum internationalen Recherchenbericht über die internationale Patentanmeldung Nr.

In diesem Anhang sind die Mitglieder der Patentfamilien der im obengenannten internationalen Recherchenbericht angeführten Patentedokumente angegeben. Diese Angaben dienen nur zur Unterrichtung und erfolgen ohne Gewähr.

ANNEX

To the International Search Report to the international Patent Application No.

PCT/US 00/14048 SAE 287198

This annex lists the patent family members relating to the patent documents cited in the above-mentioned search report.

The European Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

ANNEXE

Au rapport de recherche international relatif à la demande de brevet international n°

La présente annexe indique les membres de la famille de brevets relatifs aux documents de brevets cités dans le rapport de recherche international visée ci-dessus. Les renseignements fournis sont donnés à titre indicatif et n'engagent pas la responsabilité de l' Office.

Im Recherchenbericht angeführte Patentedokumente Patent document cited in search report Document de brevet cité dans le rapport de recherche	Datum der Veröffentlichung Publication date Date de publication	Mitglied(er) der Patentfamilie Patent family member(s) Membre(s) de la famille de brevets	Datum der Veröffentlichung Publication date Date de publication
US A 5831108	03-11-1998	AU A1 66883/96	05-03-1997
		CN A 1198752	11-11-1998
		EP A1 842200	20-05-1998
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		JP T2 11510807	21-09-1999
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